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# EVALUATION OF SHIPBOARD FORMATION OF A NEUROTOXICANT (TRIMETHYLOLPROPANE PHOSPHATE) FROM THERMAL DECOMPOSITION OF SYNTHETIC AIRCRAFT ENGINE LUBRICANT

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MIL-L-23699 lubricants that are composed principally of trimethylolpropane triheptanoate (TMP) and tricresyl phosphate (TCP) have been shown to form a neurotoxicant, trimethylolpropane phosphate (TMPP), during pyrolysis and/or combustion. Mechanistically, TMPP is thought to irreversibly inhibit the GABA-mediated inhibitory response and thereby produce epileptiform clonic/tonic seizures with convulsions followed by death. Thermal decomposition of

MIL-L-23699 lubricant produces TMPP under laboratory conditions, but this product has not been detected in the workplace following actual fires. This study has examined whether TMPP is produced during an actual shipboard fire by placing the synthetic lubricant in a fire environment aboard the ex-U.S.S. Shadwell, Mobile, Alabama. Both biological and chemical analyses were performed on the thermally decomposed lubricant to ensure detection of the neurotoxic material. Under the conditions of this study, the formation of TMPP during a shipboard fire was confirmed. The implications of this finding for safe management of post-fire cleanup are discussed.

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**S**ynthetic lubricants available under Military Specification L-23699 (MIL-L-23699) are widely used in gas turbine engines of military as well as civilian aircraft. Depending on the manufacturer, the lubricant is prepared with a base stock of a polyol ester of trimethylolpropane (TMP) and/or pentaerythritol. A lubricity additive and metal deactivator is included (usually at a 1-3% concentration) to prevent interaction of the lubricant with the engine surfaces. This additive is often an organic phosphate (typically triaryl, most frequently tricresyl). The polyol ester

component of the base stock may be varied to change the viscosity of the lubricant.

Thermal decomposition of MIL-L-23699, which contains the TMP ester base stock, can produce the potent neurotoxicant trimethylolpropane phosphate (TMPP).<sup>(1,2,3)</sup> The structure of this compound is shown in Figure 1. Those formulations of MIL-L-23699 that do not contain the TMP base stock or that do not contain a phosphate additive will not produce TMPP during thermal decomposition.<sup>(2)</sup> The highly neurotoxic effect of TMPP (chemically, 4-ethyl-1-oxo-2,6,7-trioxo-1-phospha-bicyclo [2. 2. 2] octane) has been known for some time<sup>(4,5)</sup> and initial investigations were in regard to pesticide formulations. Its formation as a product of thermal decomposition was first discovered following combustion of an experimental laboratory formulation consisting of a rigid polyurethane foam containing a phosphate-derived fire retardant.<sup>(6)</sup> TMPP characteristically causes grand mal-type epileptiform clonic/tonic seizures with convulsions, followed by death. Initial observations further suggest that the TMPP mechanism of action is related to its effectiveness as an antagonist of gamma-aminobutyric acid (GABA) receptors.<sup>(7)</sup> The acute toxicity of TMPP was demonstrated for both rats and mice in this laboratory.<sup>(2,3)</sup>

The most likely routes of exposure to TMPP for personnel working around the thermally degraded lubricant are inhalation and dermal absorption. TMPP was not formed in these lubricants under normal or excessive use conditions.<sup>(2)</sup> Whether TMPP is an inhalation hazard following decomposition of MIL-L-23699 has been addressed in two previous studies in different laboratories.<sup>(8,9)</sup> In both studies rats exposed to smoke generated by pyrolysis of MIL-L-23699 showed no signs of neurotoxic insult during a 30-minute exposure using a Federal Aviation Administration (FAA) combustion chamber. The design of the FAA combustion chamber used a tube furnace for the heat source, which was physically separated from the exposure chamber by a distance of 10 to 12 inches. The furnace and chamber were connected and the atmosphere delivered by a glass tube (1" i.d.). Across the distance from furnace to chamber, the temperature dropped from > 500 °C to 40 to 60 °C. Therefore, a possible explanation for lack of toxicity from these inhalation exposures may be that the toxicant precipitates or condenses quickly out of the respirable atmosphere once it passes from the heat source to cooler ambient temperatures. These findings were preliminary and used "time to incapacitation" and "time to death" as indices of toxicity. Further characterization of the inhalation hazard needs to be performed using more sensitive indices of toxicity such as analysis of electroencephalograms (EEG). In another inhalation study that exposed rats to TMPP, the neurotoxicant was produced as a thermal decomposition product of fire-retarded polyurethane foam. Animals were exposed by suspending them over a cup furnace and alteration of EEG was demonstrated at inhaled TMPP concentrations that were insufficient to produce observable tremors.<sup>(6)</sup>

Since TMPP produced from thermal decomposition of lubricants seems to precipitate from the atmosphere at ambient temperatures, perhaps of greater concern than the inhala-

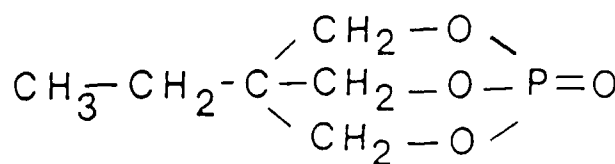


FIGURE 1. Molecular structure of trimethylolpropane phosphate (TMPP)

tion hazard is the potential for acute toxicity through dermal exposure. Mice dermally exposed to thermally decomposed lubricant developed convulsive seizures.<sup>(3)</sup> This finding suggests that a hazard may exist for clean-up personnel after a fire involving MIL-L-23699 lubricant, either as a result of the crash and burn of an aircraft, or of a fire where this lubricant is stored and/or used.

Synthetic engine lubricants containing TMP esters and TCP are likely to be found wherever such engines are used. In addition to the aviation uses referred to above, both shore activities and ships use these engines in various applications. Aboard Naval vessels, they are used to generate electrical power for all internal uses, and an increasing number of surface combatants use large turbines as their main propulsion source. Public utilities are adopting large turbines to supplement base-load capacity for use in meeting peak power demands. Finally, new uses for these high-temperature synthetic lubricants have recently been found by Air Force laboratories, thus increasing the probability of their deployment in military aircraft. In reaction to these new developments a warning message, based on previous findings of neurotoxicity, has been released regarding the use of synthetic lubricants at temperatures that may cause their thermal degradation.<sup>(10)</sup>

Thermal decomposition of MIL-L-23699 has been shown to produce TMPP under laboratory conditions, but this neurotoxicant has not been detected in the work place following actual fires. Whether personnel involved in post-fire clean up operations involving these synthetic lubricants are at risk of exposure has therefore not been established. The objective of this study was to assess whether TMPP is formed from combustion of the MIL-L-23699 synthetic lubricant (TMP ester base stock) during an actual fire aboard ship by placing the lubricant in a fire environment aboard the ex-U.S.S. Shadwell. The conditions needed for optimum formation of TMPP were determined in laboratory studies and then applied to the shipboard environment.

## MATERIALS AND METHODS

### Chemicals

#### Lubricant

The synthetic lubricant evaluated in this study was provided by the Aero Propulsion Laboratory, Fuels and Lubricants Division, Wright-Patterson Air Force Base, Ohio. This lubricant, which was used in both laboratory and shipboard

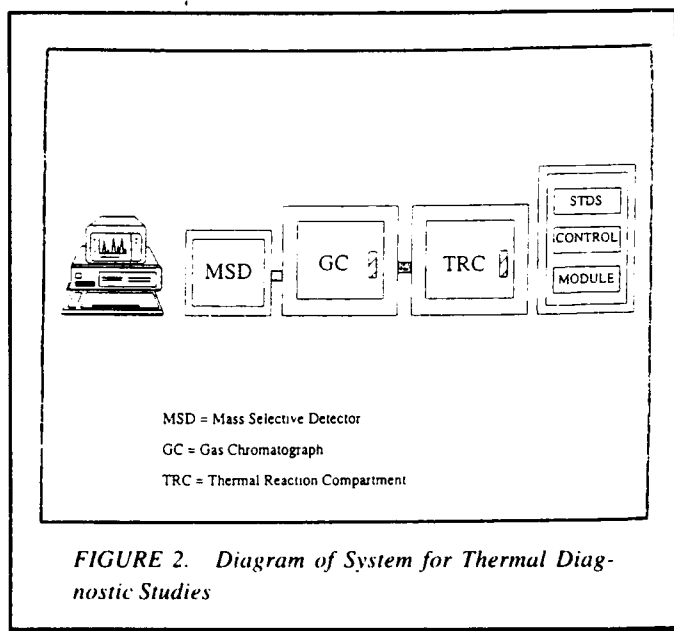


FIGURE 2. Diagram of System for Thermal Diagnostic Studies

studies, was selected from the qualified products available under Military Specification MIL-L-23699 and was known to have the trimethylolpropane carboxylic acid ester base stock formulation containing an organophosphate additive. The specific composition of the lubricant used is proprietary information and cannot be reported. Gas chromatographic analyses (described below) of the nonthermally degraded lubricant demonstrated the absence of TMPP prior to thermal treatments.

#### Authentic standard

A standard of TMPP was needed to allow identification of the neurotoxicant in the thermally decomposed lubricant. This standard was prepared using methods previously described,<sup>(11,12)</sup> and the synthesized standard authenticated by previously described electron impact mass fragmentation patterns<sup>(13)</sup> and melting-point analysis. All other chemicals used in this study were of reagent grade quality.

#### Laboratory Studies

Formation of TMPP during thermal decomposition of MIL L 23699 lubricant was characterized in the laboratory over a temperature range of 300 to 800 °C using a System for Thermal Diagnostic Studies (STDS) instrument. This instrument was developed at the University of Dayton Research Institute, Dayton, Ohio, and was marketed as the Model

1000 System. This analytical instrumentation (schematically shown in Figure 2) is composed of a thermal reaction compartment consisting of a modified Lindberg furnace and quartz reaction cell with associated flow and temperature controllers, a 5890 Hewlett-Packard (Hewlett Packard Co., Avondale, Penn.) gas chromatograph, a 5970B Hewlett-Packard mass selective detector (MSD), and a 59970 MS Hewlett-Packard ChemStation with associated gas chromatographic software and a mass spectral library. The conditions used for the thermal reaction compartment, the gas chromatograph, and the MSD are listed in Table I.

Typically, the lubricant sample was prepared in toluene and injected onto a quartz wool injector that had been equilibrated at 100 °C. After allowing time for the more volatile solvent to be removed from the lubricant, the thermal reaction compartment was rapidly heated from 100 to 300 °C, causing the sample to pass into the reaction cell. The residence time of the sample in the reaction cell (i.e., period of thermal decomposition) was maintained at 5 sec for each sample by adjusting the temperature and flow rate of the carrier gas. Residual sample and decomposition products were cryogenically focused at the head of the gas chromatographic column at -50 °C. The sample was then fractionated by gas chromatography and the degradation products identified by Selective Ion Monitoring with a Mass Selective Detector. The gas chromatographic temperature program was the same for all samples. To determine the formation of TMPP under conditions of combustion and pyrolysis, reaction cell gases of air and helium were used, respectively.

The stability of authentic TMPP, free of lubricant components, was evaluated using the same conditions and parameters as those for the MIL-L-23699 lubricant, except TMPP was prepared in methanol and the reaction cell gas was limited to air only. The injection volume was 4 µL (5%

TABLE I. Thermal Diagnostic System Conditions and Operating Parameters

Thermal Reaction Compartment (TRC)	
TRC Oven:	100 °C to 300 °C at 25 °C/min
TRC Injector:	225 °C
Lindberg Furnace:	300 °C to 800 °C
Sample Size:	0.5 µL
Sample Residence Time:	5 sec
TRC to GC Transfer Line:	300 °C
Gas Chromatograph (GC)	
Initial Temperature:	-50 °C
Temperature Program Rate:	8 °C/min
Final Temperature:	300 °C
GC to MSD Transfer Line:	320 °C
Column:	30 m DB5, 0.25 mm ID, 0.1 µm film thickness
Carrier gas:	Helium
Mass Selective Detector (MSD)	
Ion Source Potential:	70 eV
Selected Ion Monitoring:	143, 150, 151, 163, 178
Scan Range:	35 to 550 amu
Scan Speed:	427 amu/sec
Resolution:	1 amu

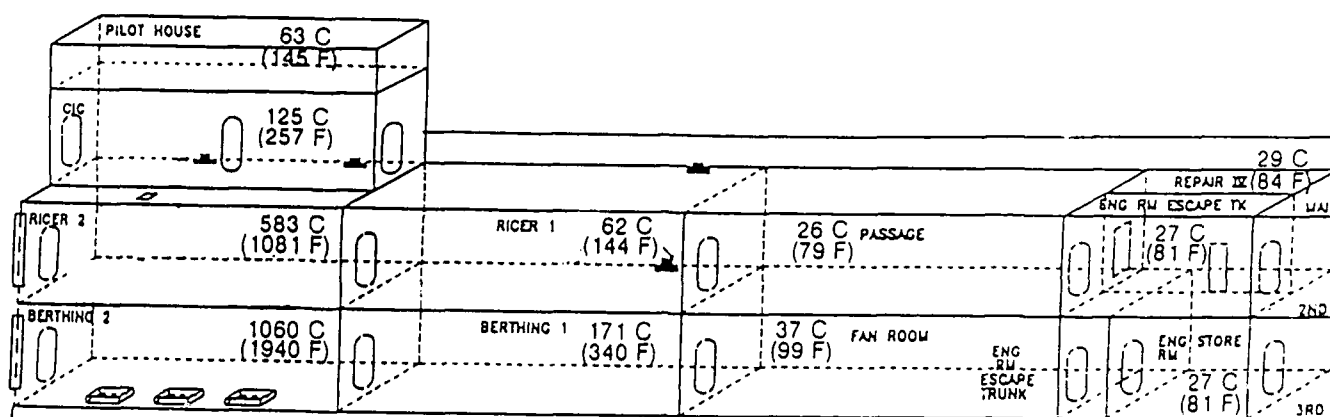


FIGURE 3. Diagram of ex-U.S.S. Shadwell's compartments showing maximum temperatures achieved in different spaces during a previous fire in Berthing 2; the lubricant storage was placed in Ricer 2.

TMPP stock solution) and the range of reaction cell temperatures was from 300 to 550 °C.

### Shipboard Tests

#### Experimental Design

Shipboard tests were conducted aboard the ex-U.S.S. Shadwell,<sup>(14)</sup> which is maintained and operated as a fire-test research vessel by the Navy Technical Center for Safety and Survivability in Mobile, Ala. A diagram of the ship's spaces for the portside wing wall where the fire was staged is shown in Figure 3. Compartments used for the study were designated as Berthing 2 and Ricer 2. The fire was created in the lower Berthing 2 compartment, with conductive heat transfer to the upper Ricer 2 compartment. Ricer 2 was chosen as the compartment to contain the lubricant based on the maximum compartment temperatures determined in previous studies (see Figure 3); the maximum temperature achieved in this compartment was 583 °C, which was close to the optimal temperature (525 °C) for TMPP formation.

A schematic drawing of the arrangement of the flammable cabinet, lubricant can, and sample collection lines is shown in Figure 4. One quart of lubricant, contained in a screw-top, rectangular metal can, was placed in Ricer 2 inside a benchtop-size flammable locker (Product No. RA 1199, Laboratory Safety Supply, Janesville, Wis.). The cabinet was set on the steel deck. This

design simulated actual storage of the lubricant at work stations aboard Naval aircraft carriers in the fleet.<sup>(15)</sup>

The flammable locker was modified (not illustrated in Figure 4) to contain calorimeters for measurement of heat flux, type K inconel-sheathed thermocouples to detect temporal changes in temperature at three locations in the cabinet, and gas sampling lines for monitoring the contents of the cabinet at different temperatures. A series of eight grab-samples were collected by remotely operated solenoid valves attached to stainless steel collection bottles located outside the compartment. In addition, a video camera was placed adjacent to the cabinet vent hole to film the condition of the can during the fire. The camera was protected in a water-cooled housing and all temperature-sensitive equipment such as

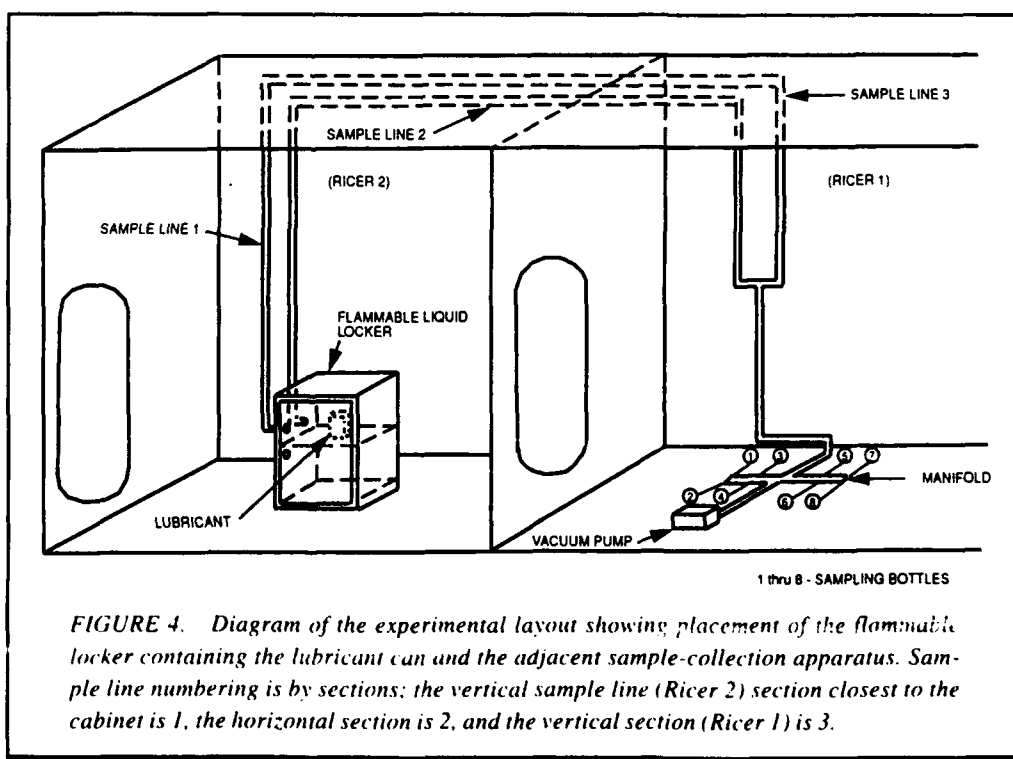


FIGURE 4. Diagram of the experimental layout showing placement of the flammable locker containing the lubricant can and the adjacent sample-collection apparatus. Sample line numbering is by sections; the vertical sample line (Ricer 2) section closest to the cabinet is 1, the horizontal section is 2, and the vertical section (Ricer 1) is 3.

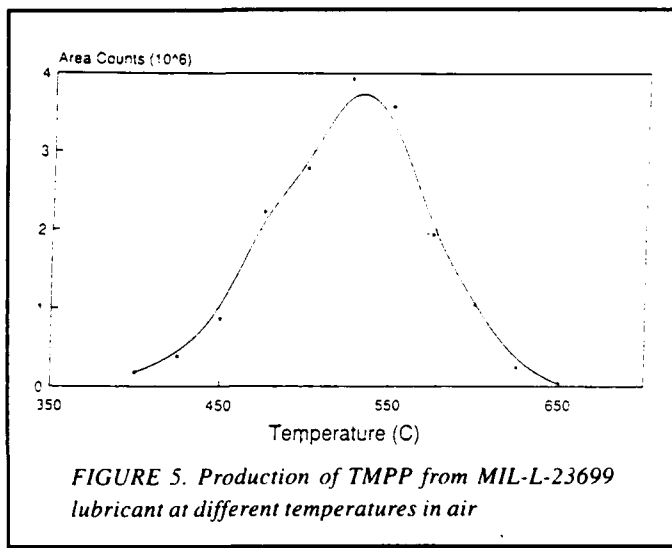


FIGURE 5. Production of TMPP from MIL-L-23699 lubricant at different temperatures in air

cables were wrapped in Fiberfax (Manville Corp., Denver, Colo.) and heat reflective aluminum foil.

The Ricer 2 compartment was similarly equipped with thermocouples for measuring temperatures outside the flammable cabinet, and with video and infrared camera equipment for monitoring the compartment environment. No combustible material except for the test material was placed in the compartment. Gas analyzers were used to continuously measure CO<sub>2</sub> and CO (infrared analyzers) and O<sub>2</sub> (paramagnetic oxygen analyzer) levels during the test.

### Conditions

To achieve the desired temperature inside the double-walled flammable cabinet, it was necessary to cut a 1 ft<sup>2</sup> (0.093 m<sup>2</sup>) hole in the deck above Berthing 2 to allow sufficient heat transfer into Ricer 2. The source of ignition of the fire in Berthing 2 was *n*-heptane (5 gallons) poured into three 4 ft<sup>2</sup> (0.37 m<sup>2</sup>) pans. Once started, the fire was maintained by remotely pumping diesel fuel into the pans. To achieve a maximum temperature inside the flammable cabinet of 515 °C, a burn time of approximately 45 min was required. The fire in Berthing 2 was extinguished within 2 min after achieving the 515 °C temperature by turning off the flow of diesel fuel. Even with water cooling of the exterior bulkheads of the compartments, a period of approximately 2 hours was required before the compartment was cool enough to allow re-entry and sample collection.

### Sample collection

Once the compartment and cabinet were cooled to ambient conditions, samples were collected from the exterior and interior of the cabinet using methanol-soaked gauze pads. The sample collection lines were sectioned into three pieces and rinsed with methanol to remove lubricant that had escaped the lubricant can. All samples, the lubricant can, and grab sample bottles were brought back to the laboratory for chemical and biological assay for TMPP. After samples had

been collected, the cabinet, compartment, and collection lines were decontaminated by treatment with 1 M NaOH. TMPP is hydrolyzed by treatment with strong alkali.

### Analysis of collected samples

All samples were extracted from their containers with methanol, filtered to remove particulate material, and the methanol removed by rotoevaporation in a water bath. The homogenous oil samples were then reconstituted in acetone (5/100 dil) for gas chromatographic analysis. All analyses were performed using a Hewlett-Packard 5890 gas chromatograph/nitrogen-phosphorous detector (GC/NPD) Chem Station (Model 7376 Autosampler) equipped with a 30 m x 0.53 mm i.d. SPB-1 (1.5 μ film thickness) fused-silica capillary column (Supelco, Inc., Bellefonte, Penn.), with splitless injection. The injector and detector temperature were 300 °C and 275 °C, respectively. The GC oven temperature used was 1 min at 50 °C, then 10 min at a gradient of 20 °C/min up to 250 °C. Quantitative analysis of TMPP in the reconstituted samples was accomplished by the external standard method. The minimum detectable level for TMPP in the present study was 1 ng/mL.

### TMPP Confirmation by Bioassay and Gas Chromatographic/Mass Spectrometric (GC/MS) Analysis

#### Bioassay

Both B6C3F1 mice and Fischer 344 rats were maintained (in separate colonies) for bioassay of neurotoxicity. These species had been used for toxicity testing with TMPP in previous investigations.<sup>(2,3)</sup> All animals were maintained in cages with water and laboratory chow provided ad libitum. Application of combusted lubricant was both dermal and by intraperitoneal injection.

#### GC/MS

Confirmation of the presence of TMPP in shipboard samples was accomplished using a Finnigan 5100 GC/MS in the electron impact mode as previously described.<sup>(2)</sup>

## RESULTS AND DISCUSSION

### Findings from the System for Thermal Diagnostic Studies (STDS)

Both formation and decomposition of TMPP in MIL-L-23699 lubricant under high temperature conditions were evaluated using the STDS (see methods). Sample residence time in the thermal reaction cell for both studies was 5 sec.

#### TMPP formation

Figure 5 depicts the production of TMPP from synthetic lubricant at varied temperatures in an air atmosphere. No attempt to quantitate actual amounts of TMPP formed was made in STDS studies; data are depicted as area counts only. Under the conditions employed, the optimum temperature

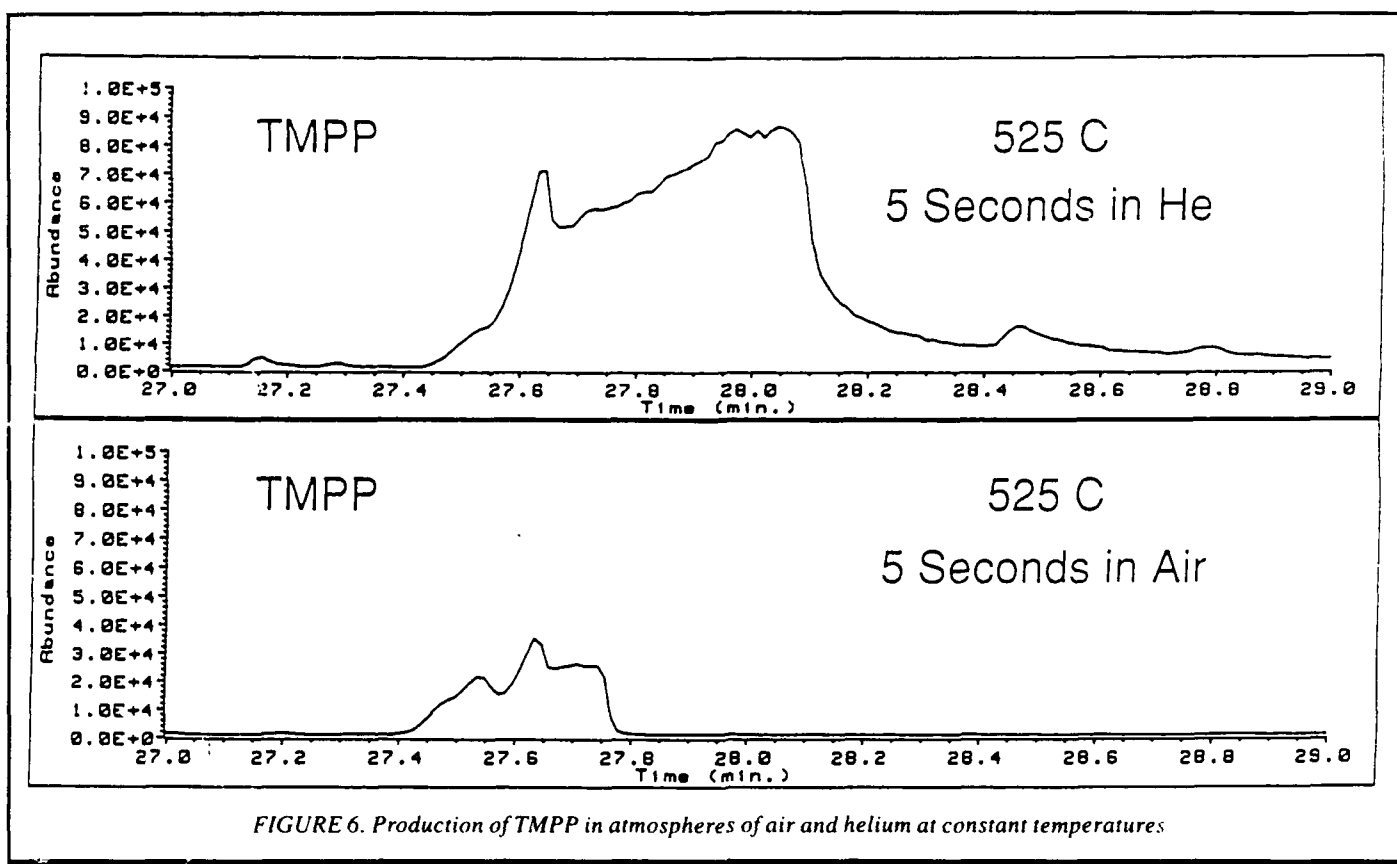


FIGURE 6. Production of TMPP in atmospheres of air and helium at constant temperatures

for formation of TMPP was approximately 525 °C, while formation of TMPP did not occur below 350 °C. These findings compare favorably with previously reported values.<sup>(2)</sup>

Comparison of TMPP formation in an oxygen (air) and nonoxygen (He) environment is depicted in Figure 6. In the absence of oxygen, the production of TMPP was approximately six-fold higher, suggesting oxidative decomposition of the compound in air atmospheres. The figure shows total ion chromatograms; the convoluted peak shapes arise from coeluting species that are not detectable in the selective ion monitoring mode. These coeluting species influence the

chemistry of the column stationary phase and therefore the resolution of the TMPP analytical peak. A scan across the retention-time range of the peak showed spectral purity.

#### Thermal stability of TMPP

The loss of TMPP from authentic standard samples (previously described<sup>(2)</sup>) in the thermal reaction cell at varied temperatures is shown in Figure 7. Temperatures above 475 °C produce very rapid decomposition of TMPP with no detectable amounts of TMPP present at 500 °C. These data seem inconsistent with data indicating maximum production at 525 °C (Figure 5) and total decomposition at 650 °C. Three possible explanations for this discrepancy are proposed. First, it may be that lubricant components provided some unknown means of protection against the elevated temperatures and thus insulated the TMPP molecule from thermal decomposition. In the absence of lubricant, the TMPP molecule received all of the thermal energy, resulting in its destruction. Secondly, the lubricant components may have provided a precursor pool for the continued formation of the TMPP product, which resulted in higher levels of the compound. Lastly, the reaction time for the formation of TMPP in lubricants may be such that it was formed at the very end of the 5 sec residence time and was removed from the cell before it could decompose. None of the possible explanations for the apparent discrepancy was investigated.

Knowing the temperatures at which formation and thermal decomposition of TMPP occurs in the lubricant matrix is

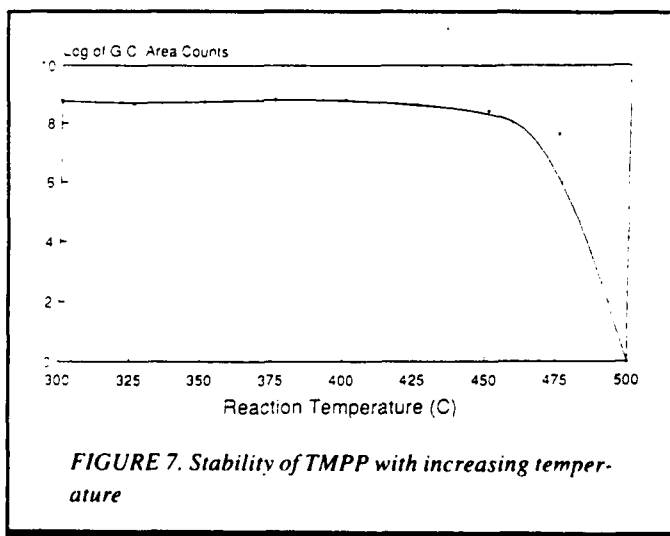


FIGURE 7. Stability of TMPP with increasing temperature

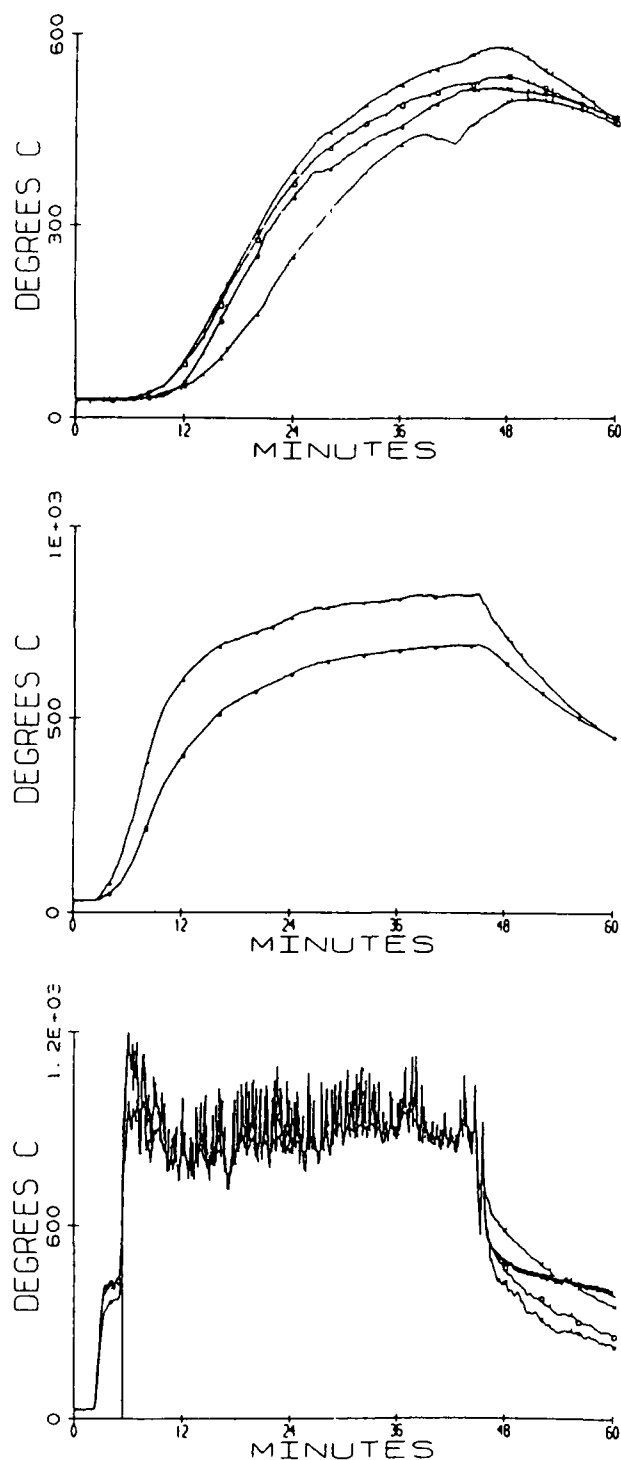


FIGURE 8. Temperature profiles for the flammable storage locker and compartments during the fire aboard the ex-U.S.S. Shadwell. Top, middle, and bottom figures represent temperatures inside the flammable storage cabinet, Ricer 2, and Berthing 2, respectively.

important from the standpoint of TMPP hazard evaluation. In this regard, our laboratory recently received an inquiry as to whether TMPP might be formed in power plants using spent synthetic lubricant as a fuel source.<sup>(16)</sup> Since the power

plant furnace temperatures were in excess of 1000 °C, the use of spent lubricant in this application was considered safe with regard to TMPP production, given that TMPP was totally decomposed at temperatures of 650 °C.

Thermal decomposition of the TMPP standard resulted in the formation of a broad-based, unresolved peak of nonchromatographable material. Within this complex mixture, two products were tentatively identified from the MS library as 3-methyl-2-methylene-3-butene-1-ol and 2,3-dimethyl-1-pentene. The amount of these substances relative to the amount of TMPP initially injected was not quantifiable.

### Shipboard Tests

Profiles of temperature versus time for the flammable cabinet and the compartments are shown in Figure 8. The interior of the flammable cabinet increased in temperature at a much slower rate than the surrounding Ricer 2 compartment. Within the compartment, the maximum temperature achieved was above 700 °C. Based on the results of laboratory studies (Figures 5 and 6), any TMPP that may have escaped into this compartment atmosphere was most probably thermally degraded to non-neurotoxic products. The percent concentration of O<sub>2</sub>, CO<sub>2</sub>, and CO within Ricer 2, as a function of time, are shown in Figure 9. The two curves shown for CO<sub>2</sub> and O<sub>2</sub> reflect two separate monitoring sites within the compartment. The source of CO<sub>2</sub> and CO was most likely the combustion of the diesel fuel used to generate the fire rather than the synthetic lubricant. Based on laboratory findings (see Figure 6), the observed decrease in percent O<sub>2</sub> concentration may have enhanced the production of TMPP.

Although the integrity of the metal can within the cabinet was maintained during the test, the lubricant escaped as a vapor through the spaces between the threads on the screw-cap top. Only a very small amount of oil (< 3.5 mL) remained in the quart can following the fire. There was no visible sign of liquid oil in or outside the cabinet, but the cabinet interior and exterior surfaces were blackened by a lubricant residue that resembled tar. The cabinet atmosphere sampling lines contained the largest amount of spent lubricant. These lines had been wrapped with insulation and foil during the fire and were flushed with methanol to extract the residual lubricant. No TMPP was found in the stainless steel collection bottles, and therefore the level of TMPP formation for any particular temperature could not be determined. The lubricant was vaporized at the high temperatures of the fire and condensed to liquid (containing TMPP) in the cooler surrounding areas (see Table II). This physical behavior is consistent with that observed in the laboratory and may help explain the lack of neurotoxicity observed in laboratory experiments with the FAA chamber (discussed above). The fact that TMPP is not found in more distant sampling areas indicates that inhalation of a vapor or suspended aerosol containing TMPP by emergency personnel is unlikely. In order to receive an inhalation exposure to TMPP, personnel would have to be in the high temperature area of the fire; the high temperature would be incompatible with life and



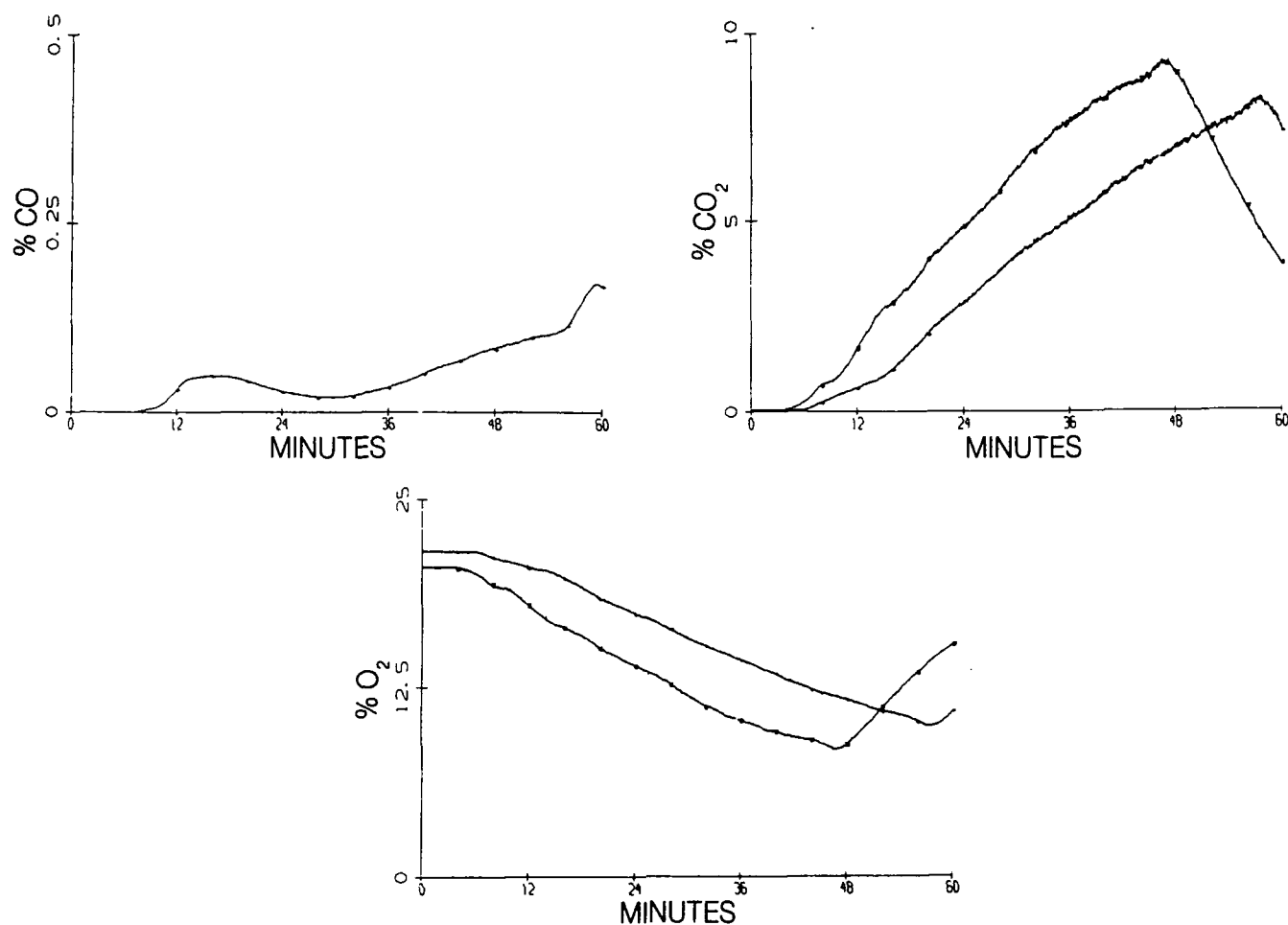


FIGURE 9. The concentration of CO, CO<sub>2</sub>, and O<sub>2</sub> concentrations in Ricer 2 as a function of time

neurotoxicity would be of little consequence. However, dermal contact with thermally decomposed products is a realistic possibility.

#### Lubricant Analysis

##### GC/NPD Analyses

Table II lists the sample collection sites, the volume of lubricant collected, and the concentration of TMPP detected (GC/NPD analysis) for the respective samples. The data depict a gradient of deposition of TMPP from high concentration (can residue) to low concentration in collection sites farther away from the original position of the unburned lubricant (see Figure 4).

##### Bioassay

An aliquot of the spent lubricant containing enough TMPP (1 mg/kg) to elicit a convulsive response was prepared for injection by dissolving it in an equal volume of dimethyl sulfoxide. The convulsive dose was calculated based on a previously reported bioassay lethal dose value of 0.5 mg/kg.<sup>(2)</sup> The DMSO dissolved sample used for bioassay

contained 1 mL of the extracted, filtered, neat residue from the can (TMPP concentration = 2.1 mg/mL). The solution was injected intraperitoneally into a male Fischer 344 rat (300 g), and the characteristic convulsions produced by TMPP were observed within 3 minutes. Control experiments in which rats were injected with DMSO or mixtures of non-decomposed lubricant dissolved in DMSO produced no neurotoxicity<sup>(2)</sup>. These experiments were not repeated for this bioassay.

TABLE II. Amounts of TMPP from Shipboard Collection Sites

Sample Site	Collection Volume (mL)	Lubricant TMPP Conc. (mg/mL)
Cabinet surface	0	None Detected
Can residue	3.5	2.1
Sampling Line 1	2.6	0.39
Sampling Line 2	2.0	0.31
Sampling Line 3	1.9	0.12
Manifold for gas collection	4.3	0.01
Approx. total volume =	14.3	

The presence of TMPP in shipboard samples was confirmed by direct comparison of their mass fragmentation patterns with those of known standards. The mass fragmentation patterns were generated in the selected ion monitoring mode, and the 149, 150, 151, 163, and 178 amu ions scanned as previously described.<sup>(2)</sup>

Bioassay and GC/MS confirmation of TMPP in the thermally degraded lubricant proved that TMPP production is possible during a shipboard fire involving the MIL-L-23699 synthetic lubricant. Should such a fire take place, the amount of TMPP formed will depend on the specific environment with regard to oxygen concentration and temperature.

### SUMMARY AND CONCLUSION

The results of this investigation demonstrated the formation of TMPP from MIL-L-23699 lubricant following a shipboard fire. In the laboratory, optimum formation occurred at approximately 525 °C in an oxygen-free atmosphere. The presence of oxygen in air appeared to limit but not prevent the formation of TMPP. The temperature range for the production of TMPP is relatively narrow (approximately 350 to 650 °C), with TMPP being destroyed at temperatures above 650 °C. In the shipboard fire, TMPP was found in samples collected from the flammable storage cabinet atmosphere and in the residual liquid in the storage can.

Many factors could influence the amount of TMPP found in the residue after a fire involving MIL-L-23699 lubricants. However, if it can be established that the lubricant was composed of a TMP-ester base fluid with a phosphate-ester additive as part of the formulation, then a reasonable presumption can be made that TMPP may be encountered during cleanup procedures. While the probability of toxic amounts of TMPP being absorbed by skin contact with contaminated residues seems remote, the grave nature of the potential consequences surely warrants the development of adequate protective and procedural measures to minimize contact, decontaminate affected spaces, and dispose of contaminated materials.

To better define and quantitate the degree of risk for ship's personnel, further studies of the conditions required for TMPP formation, the limitations for spread of the neurotoxicant, the toxic effects produced by less than lethal amounts, and the logistics of use (units of issue, amounts on board, and whether other applications of the formulation are active) of MIL-L-23699 lubricant are required.

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1. Kalman, D.A., K.J. Voorhees, D. Osborne, and I.N. Einhorn: Production of a bicyclic phosphite neurotoxic agent during pyrolysis of synthetic lubricant oil. *J. Fire Sci.* 3:322-329 (1985).
2. Wyman, J.F., M. Porvaznik, P. Servé, D. Hobson, and D.E. Uddin: High temperature decomposition of military specification L-23699 synthetic aircraft lubricants. *J. Fire Sci.* 5:162-177 (1987).
3. Porvaznik, M., J.F. Wyman, P. Servé, and D. Uddin: Evaluation of the acute dermal toxicity of a thermally decomposed military specification L-23699 synthetic lubricant. *J. Toxicol. Cut. Ocular Toxicol.* 6(4):299-308 (1987).
4. Bellet, E.M. and J.E. Casida: Bicyclic phosphorous esters: high toxicity without cholinesterase inhibition. *Science* 182:1135-1136 (1973).
5. Milbrath, D.S., J.L. Engel, J.G. Verkade, and J.E. Casida: Structure-toxicity relationships of 1-substituted-4-alkyl-2,6,7-trioxabicyclo [2. 2. 2] octanes. *Toxicol. Appl. Pharmacol.* 47:287-293 (1973).
6. Petajan, J.H., K.J. Voorhees, S.C. Packam, R.C. Baldwin, I.N. Einhorn, M.L. Grunnet, and M.M. Birkey: Extreme toxicity from combustion products of a fire-retarded polyurethane foam. *Science* 187:742-744 (1975).
7. Higgins, G.M. and R.W. Gardier: Gamma aminobutyric acid antagonism produced by an organophosphate-containing combustion product. *Toxicol. Appl. Pharmacol.* 105:103-112 (1990).
8. Crane, C.R., D.C. Sanders, B.R. Endecott, and J.K. Abbot: Inhalation toxicology: III. Evaluation of thermal degradation products from aircraft and automobile engine oils, aircraft hydraulic fluid, and mineral oil. (Report no. FAA-AM-83-12) Washington, D.C.: Federal Aviation Administration, 1983.
9. Forrest, V.J., J.F. Wyman, C.J. Hixson, J.R. Cooper, L.H. Lee, J.A. Rivera, and D.A. Macys: Combustion toxicity of an aircraft lubricant. *The Toxicol.* 9(567):142 (1989).
10. Centers, P.W.: "Warning! Neurotoxin formation in thermally degraded mixtures of trimethylolpropane esters (TMPE) of carboxylic acids and tricresylphosphate (TCP) or lubricants formulated from those materials." Aero Propulsion and Power Directorate, Wright Laboratory, WL/POSL, Wright-Patterson AFB, OH (1991).
11. Verkade, J.G. and L.T. Reynolds: The synthesis of a novel ester of phosphorous and arsenic. *J. Org. Chem.* 25:663-664 (1960).
12. Wadsworth, W.S., Jr. and W.D. Emmons: Bicyclic Phosphites. *J. Amer. Chem. Soc.* 84:610-617 (1962).
13. Kenttamaa, H. and J. Enquist: Electron impact induced fragmentation of 4-alkyl derivatives of 2,6,7-trioxa-1-phosphabicyclo [2. 2. 2] octane and the corresponding 1-oxides, 1-sulfides, and 1-selenides. *Org. Mass. Spect.* 15:520-525 (1980).
14. Williams, F. W. and H.W. Carhart: The ex-Shadwell full-scale fire research and test ship. (NRL Memorandum Report 6074) Naval Research Laboratory, 4555 Overlook Ave, Code 6183, Washington, D.C. 20375-5342.
15. von Sickle, CDR.: J. F. Wyman [Private Conversation]. Air Intermediate Maintenance Dept., U.S.S. Carl Vinson (CVN 70), San Diego, CA.
16. Rodrick, D.: "Use of Jet Aircraft Engine Lubricants as a Fuel Source for Boilers". 7 July 1992. [Private Conversation]. Navy Environmental Health Center, 2510 Walmer Ave., Norfolk, VA 23513-2617.